English Translation of

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Translucent or Opaque Glass-Ceramic Containing β-quartz Solid Solution as the Predominant Crystal Phase, and the Use Thereof

Translucent or opaque glass-ceramic containing β-quartz solid solution as the predominant crystal phase, and the use thereof

The invention relates to a translucent or opaque glass-ceramic containing β-quartz solid solution as the predominant crystal phase, and to the use thereof.

Glass-ceramics containing β-quartz solid solutions as the predominant crystal phase are known.

Thus, US Patent 4,461,839 describes transparent, translucent and opaque glass-ceramics comprising the Li_2O-Al_2O_3-SiO_2 system (so-called LAS glass-ceramics) containing β-quartz solid solution as the predominant crystal phase, where the glass-ceramics have inherent colours of from black via brown to red. However, the optical appearance has been assessed by purely visual means.

Heatable plates of glass-ceramic intended for use as cooking hobs must withstand exposure to temperatures of significantly above 300°C, in some cases above 500°C, depending on the heating system used. For testing whether a glass-ceramic is suitable for use, for example, as a cooking hob, the determination of the coefficient of linear thermal expansion for the temperature range of from 20°C to 700°C, $\alpha_{20-700°C}$, inter alia, has become established. Although glass-ceramics having a coefficient of expansion $\alpha_{20-700°C}$ of $\sim 1 \cdot 10^{-6}$/K are in principle suitable as cooking hobs, today's standard of heating systems and temperatures in the region above 500°C in the vicinity of the cooking zones (alongside the areas close to room temperature) mean that the requirement for low thermal expansion has risen to a coefficient of expansion $\alpha_{20-700°C}$ of $< 0.5 \cdot 10^{-6}$/K, ideally even $\alpha_{20-700°C} < 0.38 \cdot 10^{-6}$/K, in order to achieve acceptable rates in the breakage failure probability. Negative coefficients of thermal

expansion are permissible to a greater extent than slightly positive ones since in this case a glass-ceramic is placed under compressive stress.

It is generally known that this low expansion can be achieved using glass-ceramics comprising the Li_2O-Al_2O_3-SiO_2 system, which has been widespread in industry for decades in various areas, for example mirror carriers for telescopes, cooking utensils and cooking hobs.

In these glass-ceramics, a distinction can be made between the principal crystal phases β-quartz solid solution (β-QSS), also known as β-eucryptite solid solution, and keatite solid solution (KSS), also known as β-spodumene solid solution. Thus, the β-QSS-LAS glass-ceramics have a lower thermal expansion than KSS glass-ceramics, whose coefficients of linear thermal expansion are in the order of $\alpha_{20-700^\circ C} \sim 1 \cdot 10^{-6}/K$. Accordingly, the principal crystal phase, β-quartz solid solution, has recently been preferred over keatite solid solution for applications which require very low expansion, for example cooking hobs.

Crystal nucleation is usually carried out using TiO_2 and/or ZrO_2.

Thus, EP 0 220 333 B1, for example, discloses a transparent, coloured glass-ceramic containing β-quartz solid solution as the predominant crystal phase, where the transparency in the visible region is essentially established by adding the nucleation agents with a proportion of 1.5 – 5.0% by weight of TiO_2 and 0 – 3.0% by weight of ZrO_2, and with a total amount of TiO_2 and ZrO_2 of from 3.5 to 5.5% by weight.

DE 43 21 373 C2 likewise discloses glass-ceramics containing β-quartz solid solution as the predominant crystal phase. These are glass-ceramics having high transmission, in particular in the wavelength range

from 2700 to 3300 nm, but also high transmission in the visible region. In order to reduce the high transmission in the visible region, which is particularly interfering on use of the glass-ceramic as a cooking hob, colouring components are added to the glass-ceramic. Glass-ceramics without colouring additives have an unchanged, high transmission in the visible region.

The object of the invention is to find a translucent or opaque glass-ceramic containing β-quartz solid solution as the predominant crystal phase and having low thermal expansion, low transmission in the visible region, even without addition of colouring components, and high heat and thermal shock resistance. Furthermore, the glass-ceramic should in addition be suitable for colouring and should be particularly suitable for use as a cooking hob, cooking utensil or stove window.

The object is achieved by a glass-ceramic according to Claim 1, where the glass-ceramic has a composition (in % by weight) of Li_2O 3 - 5, Na_2O 0 - 1, K_2O 0 - 1, $Na_2O + K_2O$ 0.2 - 2, MgO 0 - 1.8, BaO 0 - 3.5, SrO 0 - 1, CaO 0 - 1, BaO + SrO + CaO 0.2 - 4, ZnO 0 - 2.8, Al_2O_3 17 - 26, SiO_2 62 - 72, TiO_2 0 - 2.5, ZrO_2 0 - 3, $TiO_2 + ZrO_2$ 1 - < 3.5, Sb_2O_3 0 - 2, As_2O_3 0 - 2, SnO 0 - < 1, P_2O_5 0 - 8, a mean coefficient of linear thermal expansion $\alpha_{20-700°C}$ of $< 0.5 \cdot 10^{-6}$/K, a mean crystal size of the β-quartz solid solution of $\geq$ $\cancel{=}$ 80 nm and a transmission (sample thickness 4 mm) $\tau_{380\,-\,780\,nm}$ of < 30%.

Overall, it is now possible to obtain a translucent or opaque glass-ceramic containing β-quartz solid solution as the predominant crystal phase which has an advantageous low transmission in the visible region, the low transmission being achieved without addition of colouring components. In addition, the glass-ceramic has an advantageous, low thermal expansion.

The fact that the total content of TiO_2 and ZrO_2 is restricted to the range from 1 to < 3.5% by weight means that, compared with known LAS glass-ceramics, only a small amount of nucleating agents is made available. The low number of nucleating agents contributes to the fact that few, but large β-quartz solid solution crystals form during the ceramicization of the glass-ceramic. The solid solution crystals grow to a mean size of greater than 80 nm. At a relatively high crystal nucleus density, many small crystals form, meaning that, owing to the resultant low crystal size, the glass-ceramic appears transparent.

The low nucleus density can be produced not only by a lower nucleating agent content, but also by process variations, in particular, for example, by shortening the nucleation time.

A further advantage of this invention is the relatively low TiO_2 content. It is known from the specialist literature that a Ti-Fe complex has a slightly colouring action. If this slight coloration is undesired, for example in transparent, white translucent or white opaque glass-ceramics, use of pure, in particular low-Fe raw materials is necessary. If the component TiO_2 is present in small amounts in the glass-ceramic, the expensive low-Fe raw materials can be omitted.

If the ZrO_2 content is selected to be greater than 3% by weight, problems occur during melting.

For fining of the glass, conventional fining agents, such as, for example, As_2O_3, Sb_2O_3, SnO_2, CeO_2, fluorides and chlorides, are used.

The H_2O content can be set in the range 0.01 - 0.05 mol/l via the choice of raw materials and

the mode of operation of the production unit (see DE 43 21 373 C2).

The glass-ceramic according to the invention preferably has a lightness value L* in the L*a*b* colour system (CIELAB system) of > 85. The glass-ceramic thus has predominantly light white shades.

The desired translucency or opacity, the low transmission in the visible region and the high lightness value - besides the composition - can be adjusted and regulated essentially via the content of nucleating agents, i.e. ZrO_2 and TiO_2, and via the mean size of the β-quartz solid solution crystals.

In order to ensure adequate meltability, at least 0.2% by weight of the non-crystal-forming alkali metal oxides Na_2O and/or K_2O are present. In order to obtain a residual glass content in the glass-ceramic in which ceramicization stresses can be relaxed, at least 0.2% by weight of the non-crystal-forming alkaline earth metal oxides BaO, SrO and/or CaO are present. The total amount of the non-crystal-forming alkali metal oxides and alkaline earth metal oxides is limited to 2% and 4% by weight respectively, since the residual glass phase is responsible for the increase in the coefficient of thermal expansion of the glass-ceramic product.

The components Li_2O, Al_2O_3, SiO_2 and, in smaller amounts, MgO and ZnO, form the β-quartz solid solution.

An Li_2O content of greater than 5% by weight results in undesired, premature crystallization during the production process.

A similar effect is exhibited by high MgO contents.

In order to avoid increased coefficients of expansion of the glass-ceramic, the MgO content is restricted to 1.8% by weight and the ZnO content to 2.8% by weight.

Al_2O_3 contents of greater than 25% by weight increase the viscosity of the glass considerably and increase the tendency towards undesired mullite crystallization. SiO_2 contents of greater than 72% by weight increase the requisite melting temperatures impermissibly.

The glass-ceramic according to the invention preferably has a composition (in % by weight) of: Li_2O 3.2 - 4.8, Na_2O 0 - 1, K_2O 0 - 1, Na_2O + K_2O 0.2 - 2, MgO 0.1 - 1.5, BaO 0 - 3.0, SrO 0 - 1, CaO 0 - 1, BaO + SrO + CaO 0.2 - 4, ZnO 0.2 - 2, Al_2O_3 18 - 24, SiO_2 63 - 70, TiO_2 0 - < 2, ZrO_2 0 - 2.5, TiO_2 + ZrO_2 1 - 3.3, Sb_2O_3 0 - 2, As_2O_3 0 - 2, SnO 0 - < 1, P_2O_5 0 - 8, a mean coefficient of linear thermal expansion $\alpha_{20-700^\circ C}$ of < $0.4 \cdot 10^{-6}$/K, a mean crystal size of the β-quartz solid solution of $\ngtr$ 85 nm and a transmission (sample thickness 4 mm) $\tau_{380-780\,nm}$ of < 30%.

The glass-ceramic according to the invention particularly preferably has a composition (in % by weight) of Li_2O 3.5 - 4.5, Na_2O 0 - 1, K_2O 0 - 1, Na_2O + K_2O 0.2 - 2, MgO 0.1 - 1.5, BaO 0 - < 3, SrO 0 - 1, CaO 0 - 1, BaO + SrO + CaO 0.2 - 4, ZnO 0.2 - < 2, Al_2O_3 18 - 22, SiO_2 64 - 68, TiO_2 0 - < 1.8, ZrO_2 0 - 2.2, TiO_2 + ZrO_2 1 - 3.2, Sb_2O_3 0 - 2, As_2O_3 0 - 2, SnO 0 - < 1, a mean coefficient of linear thermal expansion of < $0.38 \cdot 10^{-6}$/K, a mean crystal size of the β-quartz solid solution of $\ngtr$ 90 nm and a transmission (sample thickness 4 mm) $\tau_{380-780\,nm}$ of < 30%.

The glass-ceramic may additionally contain at least one colouring component, in particular CoO, Cr_2O_3, CeO_2, CuO, Fe_2O_3, MnO, NiO and/or V_2O_5, and, if desired, further colouring compounds. Owing to the said properties of the glass-ceramic, in particular the high

lightness value L*, particularly pure hues are obtained through addition of colouring components.

The glass-ceramic is preferably ceramicized at below 950°C. Above 950°C, the formation or conversion into a glass-ceramic containing keatite solid solution as the predominant crystal phase takes place, this being associated with an undesired increase in the thermal expansion.

The conversion of the glassy starting material into a glass-ceramic should likewise take place at below 950°C for economic reasons.

The glass-ceramic according to the invention is preferably used as a heatable plate for cooking and grilling, as a cooking utensil, as a stove window and as a base plate for microwave ovens.

The following examples illustrate the invention.

Table 1 shows compositions and some properties of glass-ceramics, Examples 1 and 2 relating to a glass-ceramic according to the invention and Example 3 relating to a glass-ceramic whose TiO_2 content and total content of the nucleating agents TiO_2 and ZrO_2 lies outside the invention.

Table 1 also shows the chroma C* ($C^* = \sqrt{(a^*)^2 + (b^*)^2}$) in the $L^*C^*h^*$ colour system. The chroma of the glass-ceramics according to invention is preferably $C^* < 5$.

The precursor glasses were melted at temperatures of about 1620°C using raw materials which are conventional in the glass industry, and fined. The shaping was carried out by conventional methods, for example casting or rolling. Castings measuring about 140 x 140 x 20 mm were cooled to room temperature in a cooling oven starting at about 660°C.

For conversion (1a) into a glass-ceramic, the glass-ceramic precursor glasses were heated to 740°C at about 5 K/min, held at this temperature for 1 hour, then heated to 890°C at about 2.5 K/min and held at this temperature for about ¼ hour. The cooling was carried out by switching off the oven heating.

Depending on the selected composition, the temperature/time profile of the conversion programme must be adjusted. In total, the conversion process takes significantly less than 18 hours.

In conversion 1b, the nucleation time was shortened to about ¼ hour. This conversion programme required less than 6 hours.

The fact that the residual glass phase remaining in the range 5-15% ensures stress relaxation in the sample prevents rejects during ceramicization.

After conversion 1a, Example 3, with 2.6% by weight of TiO_2, which reflects a typical composition of conventional, transparent β-QSS glass-ceramics, exhibits high transparency. In order to produce the desired translucency, a second conversion (2) is necessary, carried out in this example at 940°C with a hold time of 2 hours (conversion 2). This sample is then already converted into a KSS glass-ceramic which has a thermal expansion $\alpha_{20-700°C}$ of significantly greater than $0.5 \cdot 10^{-6}$/K.

The thermal expansion, inter alia, of the ceramicized sample was measured on the rods with a length of 100 mm and their transmission was measured on samples with a thickness of 4 mm which were polished on both sides. The sample was positioned directly at the inlet of a 60 mm integration ball. The degree of light

transmission t_{vis} (380-780 nm) is given in accordance with DIN 5033.

The principal crystal phase and the mean crystallite size were determined by X-ray diffraction diffractometry.

Table 1 Composition and properties of glass-ceramics according to the invention (Examples 1 and 2) and of a comparative glass-ceramic (Example 3)

Oxides [% by wt.]	Example 1	Example 2	Example 3
SiO_2	67.3	65.45	67
Al_2O_3	20.2	21.6	20.2
Li_2O	4.1	3.7	4.0
Na_2O	0.5	0.5	0.5
BaO	0.8	2.0	0.8
MgO	0.7	0.5	0.5
ZnO	1.7	1.75	1.6
TiO_2	1.0	1.0	2.6
ZrO_2	1.7	1.75	1.7
As_2O_3	1.9	1.85	1.2
Conversion 1a			
τ_{VIS} [%], 4 mm	7		86.5
$\alpha_{20-700°C}$ [$*10^{-6}$/K]	-0.36		-0.54
Principal crystal phase	β-QSS		β-QSS
Mean crystal size	about 110 nm		about 45 nm
L*	93.2		not measured
C*	4.2		not measured
Conversion 1b			
τ_{VIS} [%], 4 mm	6	19	
$\alpha_{20-700°C}$ [$*10^{-6}$/K]	-0.36	0.06	
Principal crystal phase	β-QSS	β-QSS	
Mean crystal size	about 125 nm	about 120 nm	
L*	93.6	not measured	
C*	4.5	not measured	
Conversion 2	omitted	omitted	
τ_{VIS} [%], 4 mm			14
$\alpha_{20-700°C}$ [$*10^{-6}$/K]			0.85
Principal crystal phase			KSS
L*			79
C*			6.9

PATENT CLAIMS

1. Translucent or opaque glass-ceramic containing β-quartz solid solution as the predominant crystal phase, having a composition (in % by weight) of:

Li_2O	3 - 5
Na_2O	0 - 1
K_2O	0 - 1
$Na_2O + K_2O$	0.2 - 2
MgO	0 - 1.8
BaO	0 - 3.5
SrO	0 - 1
CaO	0 - 1
$BaO + SrO + CaO$	0.2 - 4
ZnO	0 - 2.8
Al_2O_3	17 - 26
SiO_2	62 - 72
TiO_2	0 - 2.5
ZrO_2	0 - 3
$TiO_2 + ZrO_2$	1 - < 3.5
Sb_2O_3	0 - 2
As_2O_3	0 - 2
SnO	0 - < 1
P_2O_5	0 - 8

a mean coefficient of linear thermal expansion $\alpha_{20-700°C}$ of $< 0.5 \cdot 10^{-6}$/K, a mean crystal size of the β-quartz solid solution of $\geq\neq$ 80 nm and a transmission (sample thickness 4 mm) $\tau_{380\ -\ 780\ nm}$ of < 30%.

2. Glass-ceramic according to Claim 1, characterized by a composition (in % by weight) of:

Li_2O	3.2 - 4.8
Na_2O	0 - 1
K_2O	0 - 1
$Na_2O + K_2O$	0.2 - 2

MgO	0.1 - 1.8
BaO	0 - 3.0
SrO	0 - 1
CaO	0 - 1
$BaO + SrO + CaO$	0.2 - 4
ZnO	0.2 - 2
Al_2O_3	18 - 24
SiO_2	63 - 70
TiO_2	0 - < 2
ZrO_2	0 - 2.5
$TiO_2 + ZrO_2$	1.0 - 3.3
Sb_2O_3	0 - 2
As_2O_3	0 - 2
SnO	0 - < 1
P_2O_5	0 - 8

a mean coefficient of linear thermal expansion $\alpha_{20-700°C}$ of $< 0.4 \cdot 10^{-6}/K$, a mean crystal size of the β-quartz solid solution of $\geqslant \neq$ 85 nm and a transmission (sample thickness 4 mm) $\tau_{380-780\ nm}$ of < 30%.

3. Glass-ceramic according to Claim 1 or 2, characterized by a composition (in % by weight) of:

Li_2O	3.5 - 4.5
Na_2O	0 - 1
K_2O	0 - 1
$Na_2O + K_2O$	0.2 - 2
MgO	0.1 - 1.5
BaO	0 - < 3
SrO	0 - 1
CaO	0 - 1
$BaO + SrO + CaO$	0.2 - 4
ZnO	0.2 - < 2
Al_2O_3	18 - 22
SiO_2	64 - 68
TiO_2	0 - < 1.8

ZrO_2	0 - 2.2
$TiO_2 + ZrO_2$	1.0 - 3.2
Sb_2O_3	0 - 2
As_2O_3	0 - 2
SnO	0 - < 1

a mean coefficient of linear thermal expansion of $< 0.38 \cdot 10^{-6}/K$, a mean crystal size of the β-quartz solid solution of $\geq\neq$ 90 nm and a transmission (sample thickness 4 mm) $\tau_{380\ -\ 780\ nm}$ of < 30%.

4. Glass-ceramic according to at least one of Claims 1 to 3, characterized in that the glass-ceramic has a lightness value L* in the L*a*b* colour system (CIELAB system) of > 85.

5. Glass-ceramic according to at least one of Claims 1 to 4, characterized in that the glass-ceramic contains at least one colouring component.

6. Glass-ceramic according to Claim 5, characterized in that the glass-ceramic contains CoO, Cr_2O_3, CeO_2, CuO, Fe_2O_3, MnO, NiO and/or V_2O_5.

7. Glass-ceramic according to at least one of Claims 1 to 6, characterized in that its ceramicization is carried out at below 950°C.

8. Use of a glass-ceramic according to Claims 1 to 7 as a heatable plate for cooking and grilling, as a cooking utensil, as a stove window or as a base plate for microwave ovens.

Abstract

The invention relates to a translucent or opaque glass-ceramic containing β-quartz solid solution as the predominant crystal phase, having a composition (in % by weight) of Li_2O 3-5, Na_2O 0-1, K_2O 0-1, $Na_2O + K_2O$ 0.2-2, MgO 0-1.8, BaO 0-3.5, SrO 0-1, CaO 0-1, BaO + SrO + CaO 0.2-4, ZnO 0-2.8, Al_2O_3 17-26, SiO_2 62-72, TiO_2 0-2.5, ZrO_2 0-3, $TiO_2 + ZrO_2$ 1-<3.5, Sb_2O_3 0-2, As_2O_3 0-2, SnO 0-<1, P_2O_5 0-8, a mean coefficient of linear thermal expansion $\alpha_{20-700°C}$ of $< 0.5 \cdot 10^{-6}$/K, a mean crystal size of the β-quartz solid solution of $\geq$ 80 nm and a transmission (sample thickness 4 mm) $\tau_{380-780\,nm}$ of < 30%. The glass-ceramic is preferably used as a heatable plate for cooking and grilling, as a cooking utensil, as a stove window or as a base plate for microwave ovens.